

# Modification of naturally occurring polymers for enhancing drilling fluid performance: A review

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## Abstract

The performance and efficiency of drilling fluids in oil and gas operations are significantly influenced by the nature and modification of their polymeric additives. This review investigates the role of naturally occurring polymers (primarily cellulose and starch) and the impact of their chemical, enzymatic, genetic, and physical modifications on drilling fluid performance. Native forms of cellulose and starch have thermal stability, solubility, and rheological performance limitations, which restrict their application in demanding wellbore environments. However, through modifications such as carboxymethylation, acetylation, succinylation (OSA), cross-linking, and oxidation, these polymers exhibit improved physicochemical properties including enhanced viscosity, reduced filtration loss, and increased temperature and salt resistance. Experimental and literature-based analyses show that cross-linked and dual-modified starches are particularly effective in high-pressure, high-temperature (HPHT) drilling conditions. At the same time, acetylated and carboxymethylated forms offer utility in moderate environments. Despite promising physicochemical profiles, oxidized starch remains underexplored for drilling applications. This review underscores the importance of polymer selection and targeted modification in designing efficient, environmentally friendly drilling fluids for various operational scenarios.

**Keywords:** Cellulose; Drilling fluid; Modification; Physicochemical properties; Rheological properties, Starch.

## 1. Introduction

Drilling fluids, also called drilling muds, are special fluids used in drilling oil and gas wells. A drilling fluid is a complex blend of water, oil, clay-based materials, and various chemical additives that circulates within a wellbore to transport cuttings to the surface [1]. Its proper formulation and performance are essential to the success of drilling operations because they serve a variety of purposes, such as bottom-hole cleaning, lubricating and a cooling agent, controlling high-pressure zones and pressure differences between the wellbore and the surrounding subsurface formations, minimizing formation damages, reducing circulation loss, and removing cuttings to the surface [2-4]. The impacts of drilling fluid cannot be overemphasized, since drilling fluid knowledge is essential for rotary drilling operations in the petroleum industry. Activities such as drilling, exploration, and production cannot be carried out without drilling or completion fluids. These fluids are therefore indispensable for both onshore and offshore oil and gas operations.

Choosing the right drilling fluid involves considering multiple factors, such as the location and nature of the formation, variations in wellbore pressure and temperature, and the properties of formation fluids, strength, porosity, and permeability. Additional considerations include production requirements, environmental impact, and safety concerns [5]. Drilling fluids are generally categorized according to their base fluid into three main types: water-based drilling fluids (WBDFs), oil-based drilling fluids (OBDFs), and synthetic-based drilling fluids (SDFs). Each type offers distinct properties and advantages, and the choice for a specific drilling operation depends on factors such as the formation

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type, drilling depth, and applicable environmental regulations [6,7]. The ability of drilling fluid to fulfill its multiple functions is largely determined by its rheological properties, which directly influence drilling efficiency, safety, and overall success. Key rheological parameters include density, viscosity, gel strength, and fluid loss. The use of drilling fluid additives, such as viscosifiers, fluid loss control agents, weighting agents, thinners, and lost circulation materials (LCMs), is also determined by the drilling conditions, formation characteristics, and regulatory requirements. [8]. The particular function to be carried out by a drilling fluid in a specific site determines its composition and the fluid to be used.

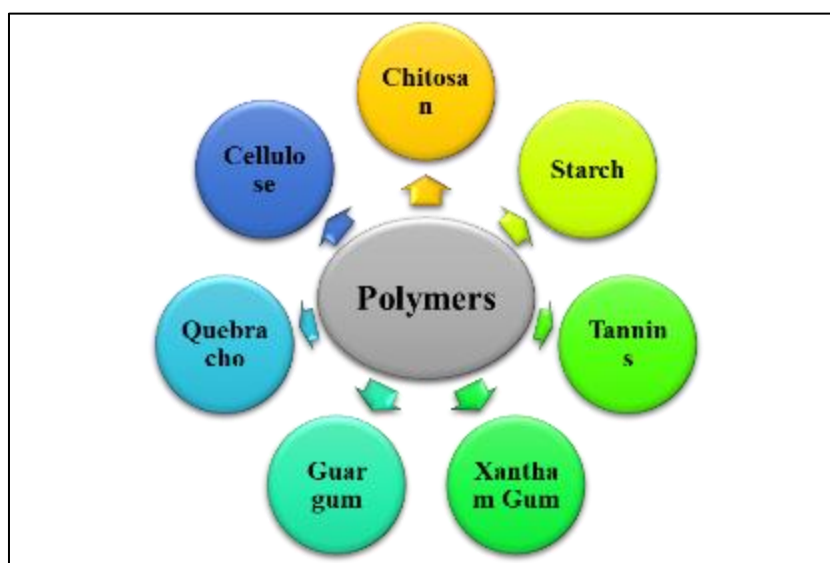
Common additives used in drilling fluid formulations include weighting agents such as barium sulphate (barite), calcium carbonate (chalk), and hematite. Viscosity is adjusted using thickeners like xanthan gum, guar gum, glycol, carboxymethylcellulose, polyanionic cellulose (PAC), nanoparticles, or starch [9]. An effective drilling fluid should maintain stable rheological properties over a wide range of pressures and temperatures while minimizing fluid loss through the formation of a thin, low-permeability filter cake [10]. Careful selection and application of these additives can enhance drilling fluid performance, reduce formation damage, and help prevent operational challenges during drilling.

### 1.1. Naturally occurring polymers for drilling fluid formulations

Polymers are a diverse group of drilling fluid additives characterized by strong hydrophilicity and high hydrodynamic volume, making them valuable for enhancing rheological properties and improving drilling fluid performance [11]. Their primary role is to upgrade the functionality of simple systems, such as clay-based muds, and to prevent bentonite flocculation.

Polymers used in drilling fluids can be classified by their chemical composition, function in drilling fluids, and origin. From a chemical standpoint, they may be anionic, nonionic, or cationic [12]. Structurally, polymers can be grouped into linear, branched-chain, and crosslinked (networked) types.

- Linear polymers consist of monomer chains and include materials such as natural rubber, elastomers, carboxymethyl cellulose, partially hydrolyzed polyacrylamide, hydroxyethyl cellulose, and other high-elasticity polymers [13–15].
- Branched-chain polymers contain side branches along the main chain, with examples including amylopectin, starch, and xanthan gum.
- Crosslinked polymers feature bonds between adjacent macromolecules, resulting in insoluble and inelastic structures. Examples include epoxy resins in their curing stage and crosslinked xanthan gum, a polysaccharide produced by *Xanthomonas campestris* [13].



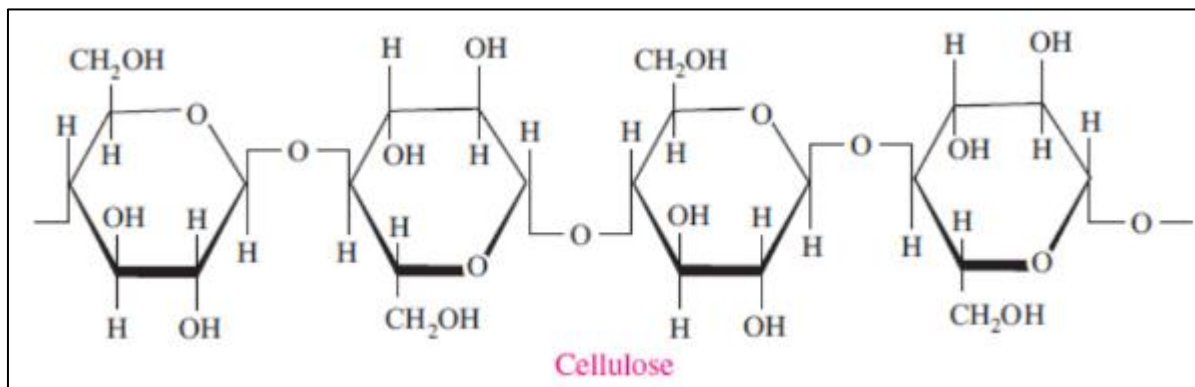
**Figure 1** Polymers for Drilling Fluid Formulation

Today, naturally occurring polymers are modified with conditions that are specifically matched to enhance the rheological characteristics of drilling fluids. In addition, polymers serve various functions, such as acting as viscosifiers,

filtration control agents, flocculants, and deflocculants. Within drilling fluids, they are incorporated as additives to mitigate sticking to pipes, corrosion inhibitors, emulsifiers, foaming agents, lubricants, and surfactants [16]. Naturally occurring polymers include Cellulose (including CMC and HEC), guar gum, polysaccharides (Chitosan), quebracho, starch, Tannins, Xanthan gum, etc. This review will, however, focus mainly on cellulose and starch as polymers for enhancing drilling fluid properties.

## 2. Cellulose

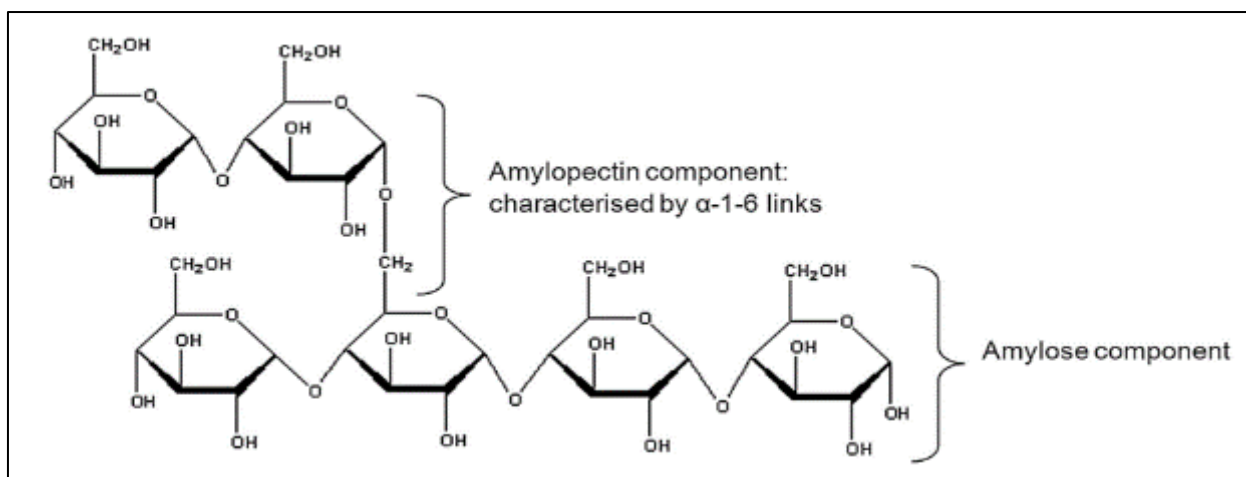
Cellulose (Figure 2), a major structural component of plant cell walls, is composed of long, unbranched chains of glucose units linked by  $\beta$ -(1 $\rightarrow$ 4) glycosidic bonds. Each chain contains approximately ten thousand glucose residues (Carpita & Gibeaut, 1993). Hydroxyl groups (-OH) protrude from the chains, allowing hydrogen bonding with adjacent chains. This extensive hydrogen bonding results in a rigid, cross-linked structure that provides high mechanical strength and renders cellulose insoluble in water. Due to the presence of  $\beta$ -(1 $\rightarrow$ 4) linkages, humans are unable to digest cellulose, as it requires the enzyme  $\beta$ -glycosidase, which is absent in the human digestive system.



**Figure 2** Structure of cellulose [16]

## 3. Starch

Starch, obtained from cereals, roots, tubers, and stems of various plants, exhibits physicochemical properties that vary with its botanical source. It is a polysaccharide composed of glucose units linked by glycosidic bonds and contains two main polymers, amylose and amylopectin, whose proportions differ depending on the starch source. Owing to its abundance, low cost, and biodegradability, starch has been widely employed in its native and modified forms as a filtration control agent in drilling muds [17–20]. As the second most abundant biomass in nature after cellulose, starch consists primarily of amylose and amylopectin (Figure 3). Amylose influences the gelling behavior of starch, as gelation results from the re-association of its linear molecular chains. In contrast, amylopectin is generally larger and highly branched, which limits polymer mobility and molecular orientation in aqueous systems. The high density of hydroxyl (-OH) groups in starch molecules imparts strong hydrophilic properties, enabling effective dispersion in water [21]. In drilling applications, starch acts as an efficient protective colloid, reducing filtration loss and enhancing fluid viscosity. It offers temperature stability up to approximately 225 °F, causes minimal viscosity increase, and effectively controls fluid loss. This functionality is primarily attributed to its ability to swell and expand through the absorption of free water [22].



**Figure 3** Starch co-polymer chain with amylose and amylopectin component (16).

### 3.1. Functional properties of starch

Starch is a highly versatile material with diverse applications, largely attributed to its compact molecular structure. Its polymeric and branched configuration results in relatively low solubility in water and a reduced capacity to absorb water and oil. Nevertheless, starch possesses excellent swelling power, strong gelatinization characteristics, and the ability to produce relatively high viscosity. It can also form thin, uniform films and demonstrates desirable pasting properties, including consistency, smoothness, and clarity [23]. Furthermore, starch readily forms complexes with iodine and offers advantageous freeze-thaw and cold storage stability, making it suitable for a wide range of food and industrial formulations. While starch is vulnerable to hydrolysis by acids and enzymes, it is resistant to moderate pressure and temperature. Nonetheless, the enzymatic digestibility values of native starches are comparatively lower [24].

### 3.2. Polymer (cellulose and starch) modification

Starch and cellulose are usually used in modified forms of drilling fluids such as carboxymethylcellulose (CMC) or carboxymethyl starch (CMS) due to their solubility in water. These modified polymers and Starch and its variants are among the most common environmentally benign drilling fluid additives used to reduce filtration loss and condition drilling fluid rheology [25]. Modified polymers are often used in the petroleum industry as water plugging and redirection agents within reservoirs, crude oil emulsion breakers, and drilling fluid treatment agents. When used to enhance the rheological properties of a drilling fluid, modified starch generally performs well in reducing filtration loss, increasing viscosity, and stabilizing wellbores during drilling [26]. Most fluid-loss controlling agents used in drilling fluid formulation are modified starches. [25]

Starch in its natural form faces several limitations that restrict its practical use. It tends to have poor resistance to shear stress, degrades when exposed to heat, and suffers from issues like retrogradation and syneresis. Additionally, its processability and solubility in common organic solvents are quite limited. To overcome these challenges and meet modern technological requirements, starch undergoes different modification techniques. These modifications are designed to improve one or more of these drawbacks, thereby increasing starch's adaptability and better aligning it with consumer expectations [27,28].

Starch has been modified through various methods in the last few decades to produce functionalities relevant to multiple industrial applications. These modifications include:

- Chemical Modification
- Enzymatic Modification
- Genetic Modification
- Physical Modification

### Chemical Modification

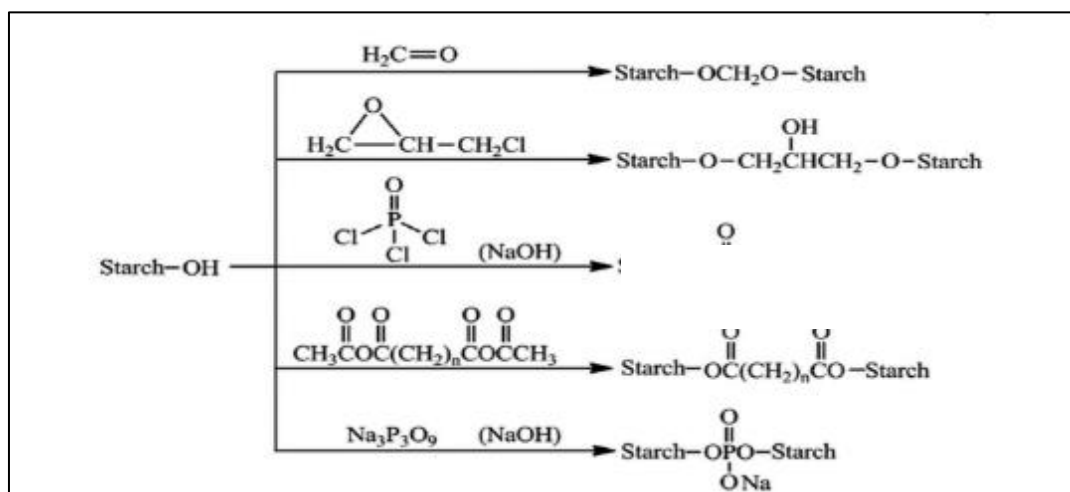
Chemical modification deals with substituting the functional groups in the starch granules. This depends on the type of substituent, distribution of substituent, degree of substitution, source of starch, and the reaction parameters such as the type of catalyst, reaction time, concentration, and pH. The different types of chemical modification include:

#### Acetylation

Chemical modification by acetylation is the most widely employed method, where functional acetyl groups are introduced by reacting with the free hydroxyl groups located on the starch polymer's branch chains to form specific esters. This process typically involves reactive reagents such as anhydrous acetic acid, vinyl acetate, or octenyl succinic anhydride (OSA), with native starch undergoing esterification in the presence of alkaline catalysts like NaOH,  $\text{Na}_2\text{CO}_3$ , KOH, or  $\text{Ca}(\text{OH})_2$  [29]. The incorporation of acetyl groups decreases the intermolecular contact resistance among starch molecules, thereby enhancing the solubility and swelling ability of acetylated starch relative to its native counterpart. Due to electrostatic repulsion forces, the formation of hydrogen bonds in acetylated starch is limited as hydroxyl groups and glucose anhydrous units are converted into acetylated groups. Acetylated starch with low degrees of substitution (0.01–0.2) finds applications in thickeners, film formers, encapsulation agents, adhesives, texturizers, and stabilizers [30].

#### Cross Linking

Cross-linking is the most commonly applied chemical modification technique, where native starch reacts with various reagents including phosphoryl chloride ( $\text{POCl}_3$ ), sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), and epichlorohydrin (ECH).  $\text{POCl}_3$  acts as an efficient crosslinking agent under alkaline conditions ( $\text{pH} > 11$ ) and in the presence of neutral salts. Among these reagents, STMP is particularly effective and widely used as a food-grade additive. Because ECH has limited water solubility and partially degrades into glycerol, water-soluble agents like  $\text{POCl}_3$  and STMP are often favored. Additionally, cross-links formed by ECH tend to be less uniformly distributed compared to those formed by STMP [31]. Cross-linked starch finds broad applications as a viscosifier and texturizer, owing to its enhanced granule stability against swelling, elevated temperatures, shear forces, and acidic environments. On the other hand, oxidized starch is characterized by low viscosity, high clarity, and poor temperature stability, while acid-hydrolyzed starch exhibits low paste viscosity, strong gel formation, and good water solubility [32]. Figure 4 provides an overview of some typical cross-linking reactions.



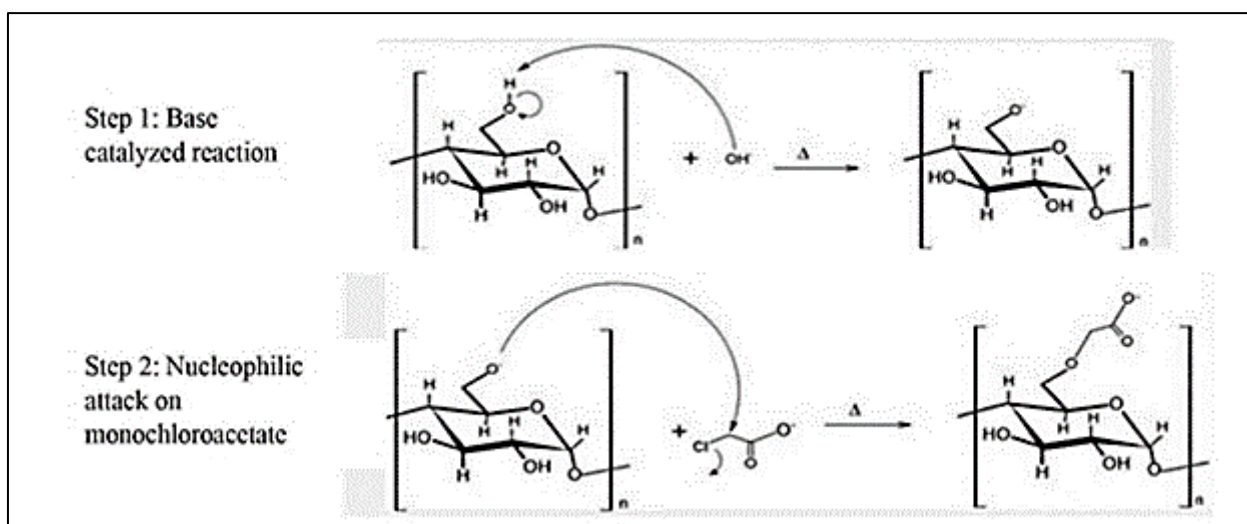
**Figure 4** Reactions of Some Commonly Used Cross-Linking Reagents (35)

#### Esterification

Starch Esterification converts the three hydroxyl groups on glucosyl residues into alkyl or aryl derivatives. A common chemical esterification method is acetylation, where hydroxyl groups are replaced by vinyl acetate or acetic anhydride in the presence of alkaline catalysts such as NaOH,  $\text{Ca}(\text{OH})_2$ , or  $\text{Na}_2\text{CO}_3$  [33,34]. Based on the degree of substitution (DS), acetylated starches are classified into three categories. Low DS starch esters (0.01–0.2) are the most prevalent and dissolve readily in cold water. Typically, by reacting acetate anhydride in an alkaline environment, starch acetates with low DS are generated, where alkali activates native starch to form a reactive intermediate called starch alkoxide, which subsequently reacts with acetic anhydride [33]. According to [35], starch esters with medium DS (0.1–0.3) exhibit lower

water solubility compared to those with low DS, while high DS starch esters (2–3) are soluble in organic solvents but insoluble in water. Acetylation primarily targets the amorphous regions and the outer lamellae of crystalline starch structures [34]. The introduction of bulky acetyl groups causes steric hindrance and structural rearrangements along the starch chains, which in turn weakens intermolecular interactions and facilitates water penetration into the granules' amorphous regions, increasing their swelling capacity. Consequently, acetylation significantly enhances the swelling power and solubility of starches derived from rice, potatoes, and corn [36]. These changes are influenced not only by DS values but also by factors such as granule size distribution, physicochemical composition, and granule rigidity. Waxy starch, which contains amylopectin with a more open structure than non-waxy starch, allows faster water infiltration, resulting in a more pronounced increase in swelling power after acetylation [37].

Another esterification approach involves modifying starch with dicarboxylic acid anhydrides like octenyl succinic anhydride (OSA). The reaction between OSA and starch produces amphiphilic OSA starches possessing both hydrophilic and hydrophobic groups, these OSA-modified starches find wide-ranging industrial uses, including in gels, films, coatings, encapsulation, and emulsification. Their desirable stability, encapsulation efficiency, interfacial activity, heat resistance, nutritional benefits, and rheological properties have recently made OSA starch a focus of considerable research interest [38].



**Figure 5** Mechanism of acetylation of starch.

#### Etherification

When hydroxypropyl groups are added to starch, hydrogen bonds in and between starch chains are broken, weakening the granular framework of the starch and increasing the starch chains' freedom of movement in amorphous regions. Propylene oxide and native starch are typically etherified with an alkaline catalyst to produce hydroxypropylated starches (HPS) [39]. Etherification decreases syneresis while boosting viscosity in starch and improving the clarity in starch paste. Consequently, it is frequently used in recipes like puddings, sauces, dipping gravies, and more. The process of esterification helps the starch to be used as an emulsion stabilizer because the starch exhibits a lower gelatinization temperature, diminished retrogradation, and less propensity to gel formation [40].

#### Oxidation

Starch oxidation involves depolymerizing starch molecules, and oxidation of starch involves incorporating carboxyl and carbonyl groups into its polymer chains. Frequently used oxidizing agents are potassium permanganate, sodium hypochlorite, hydrogen peroxide, and persulfate. The characteristics of the resulting oxidized starch derivatives depend largely on the specific oxidation method and the reagents applied [41]. This oxidation predominantly targets the hydroxyl groups at the C-2, C-3, and C-6 positions of the D-glucopyranosyl unit. Compared to native starch, oxidized starch typically shows reduced molecular weight, enhanced paste stability, and improved film-forming characteristics. It also has a lower viscosity [42].

#### Enzymatic Modification

Enzymatic modification of starch primarily aims to reduce molecular weight and debranch amylopectin, thereby enhancing the production of resistant starch. Common enzymes involved in this process include  $\alpha$ -amylase (AM),  $\beta$ -amylase,



glucoamylase, debranching enzymes, cyclodextrin glycosyltransferase, and glucose isomerase [43]. Starch enzymatic hydrolysis can be carried out through various pathways.

This green modification technique has diverse applications in the food industry. Besides improving resistant starch, utilizing these enzymes to create viscous and stable starch solutions for textile sizing applications, clarifying fruit juices and beer by removing haze, pretreating animal feed to increase digestibility, and facilitating starch saccharification or liquefaction [44]. Porous starch can be produced using fungal enzymes such as amyloglucosidase (AMG) or  $\alpha$ -amylase (AM). Pullulanase plays a key role in starch saccharification and is widely utilized in manufacturing high-glucose and high-maltose syrups.

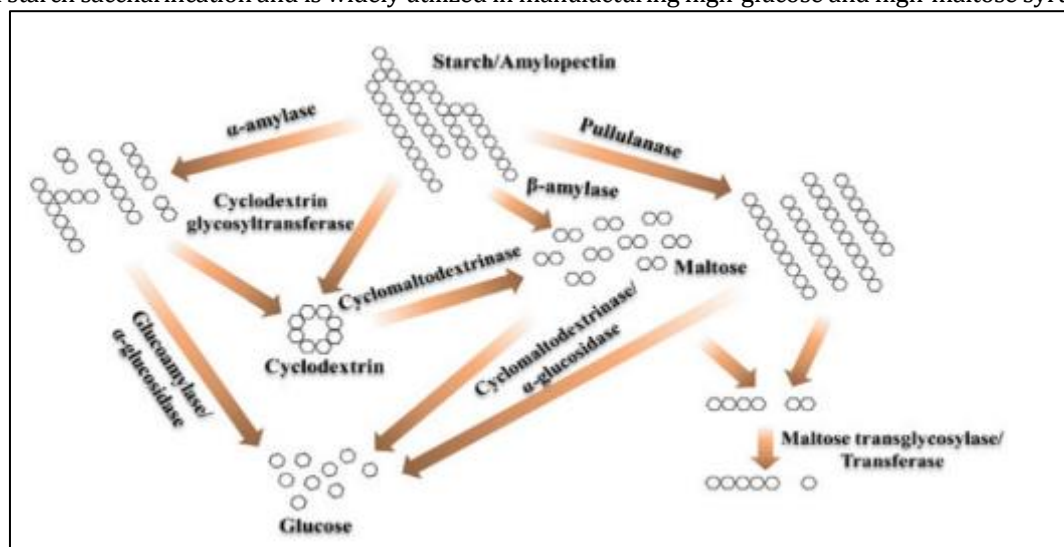


Figure 6 Enzymatic Modification of Starch [44]

### Debranching Enzymes

Examples of debranching enzymes include isoamylase and type I pullulanase, both capable of hydrolyzing  $\alpha$ -(1,6) glycosidic bonds. These enzymes break down amylopectin into linear glucans. Pullulanase specifically targets the  $\alpha$ -(1,6) glucosidic linkages present in starch, amylopectin, pullulan, and related oligosaccharides, efficiently converting branched polysaccharides into fermentable sugars during saccharification. Isoamylase, in contrast, hydrolyzes only the  $\alpha$ -(1,6) bonds within amylopectin [43].

### Endo- and Exo-Amylases

**$\alpha$ -Amylase (1,4- $\alpha$ -D-glucan glucanohydrolase)** is an endo-amylase that cleaves internal  $\alpha$ -(1,4) glycosidic bonds within starch chains, leading to a rapid reduction in molecular size. The pore size formed on starch granule surfaces depends on both the type and concentration of  $\alpha$ -amylase used [46]. **Exo-amylases** include enzymes such as glucoamylase (also known as amyloglucosidase, AMG) and  $\beta$ -amylase (1,4- $\alpha$ -D-glucan maltohydrolase), which convert maltose from the  $\alpha$ - to the  $\beta$ -anomeric configuration. These enzymes either selectively cleave  $\alpha$ -(1,4) glycosidic bonds, as  $\beta$ -amylase does, or cleave both  $\alpha$ -(1,4) and  $\alpha$ -(1,6) bonds from the nonreducing ends of starch chains, as seen with AMG and  $\alpha$ -glucosidase. Acting on the outer glucose residues of amylose or amylopectin, glucoamylase and  $\alpha$ -glucosidase release glucose, while  $\beta$ -amylase produces maltose and  $\beta$ -limit dextrin [43].

### Transferases

Function by hydrolyzing the  $\alpha$ -(1,4) glycosidic bond of a donor molecule and transferring the released residue to a glycosidic acceptor, thereby forming a new glycosidic bond. Enzymes such as cyclodextrin glycosyltransferase and amylomaltase catalyze the formation of these new  $\alpha$ -(1,4) linkages.

### 3.3. Physical Modification

Physical modification refers to the processes applied to starch that do not undergo a chemical reaction or cause the starch polymer's D-glucopyranosyl building blocks to break down. These methods include thermal, mechanical force, or physical fields. The three main types of physical modification of starch are treatments involving hydrothermal

processes, physical field applications, and various other physical approaches. Depending on the degree of modification, starch functionality frequently changes differently following physical alteration [45].

Physical modifications are known to be green and efficient. It has been used widely to prepare various foods such as noodles, fufu, biscuits, meat pies, snacks, and environmentally friendly edible films. Ultra-high pressure (UHP) treatment lowers the viscosity and starch swelling, while ultrasound affects how granules and pastes swell. Microwave modification alters the morphology and crystallinity of the starch [46]. Starch granules can also be physically altered through extrusion and milling.

**Table 1** Physical Modification of Starch

Hydrothermal Treatment	Physical Field Treatment	Other Physical Treatments
Annealing Treatment (ANN)	Microwave	Cold Plasma
	Irradiation	Drum Drying
Heat Moisture Treatment (HMT)	Pulse Electric Field (PEF)	Extrusion
	Ultra-High Pressure (UHP)	Freezing-Thawing
	Ultrasonic	Milling

### 3.4. Impacts of modification on physicochemical properties of polymers

Effects of various modification methods on the physicochemical properties of starch are summarized in Table 2. This table outlines how different chemical modifications of starch, such as carboxymethylation, acetylation, succinylation (OSA), oxidation, and cross-linking, affect key physicochemical properties like crystallinity, gelatinization, swelling, paste clarity, and thermal stability. These alterations affect the starch's thermal behavior, morphology, hydration, and stability, all of which influence their utility in drilling operations.

**Table 2** Effect of Starch Modifications on Physicochemical Properties

Modification	Crystallinity	Morphology	Gelatinization (To, Tp, Tc, ΔH)	Swelling & Solubility	Paste Clarity	Thermal / Processing Stability	Retrogradation / Storage Stability	References
Carboxymethylation	Decreases crystallinity due to disruption of H-bonds	Rough surface, partial deformation	Decreases To/Tp, ΔH due to increased hydration and chain mobility	Increases swelling and solubility due to hydrophilic groups	Increases clarity, transparent films	Increases microbial and thermal stability	Enhances reduced retrogradation due to steric hindrance	[17,23]
Acetylation	Reduces crystallinity due to substitution on hydroxyl groups	Slight roughening, granules retained	Reduces gelatinization temp and ΔH; less energy needed for swelling	Increases swelling and solubility	Enhances more transparent pastes	Improves freeze-thaw stability and viscosity control	Reduced syneresis, delayed retrogradation	[47,48]
Succinylation (OSA)	Reduced due to repulsion and molecular	Smooth to slightly porous surfaces	Improves gelatinization temp, slight ΔH changes	Improves swelling, water-holding, and	Improves clarity	Increases cold-storage and freeze-	Enhances storage stability, lowers retrogradation	[49,50]



	rearrangement			emulsifying ability		thaw stability		
Oxidation	Decreased due to depolymerization of amylose/amylopectin	Pitted, porous granules	Can go either way, To/Tp, depending on starch source; $\Delta H$ may increase	Increases solubility; better cold solubility	Improved clarity	Enhances flexibility and tensile strength in films	Improved retrogradation resistance	[51]
Cross-linking	increase or unchanged (preserved crystallinity)	Compact, roughened granules	Enhances To/Tp/Tc, lower $\Delta H$ ; more thermally stable granules	Reduces swelling and solubility (restricted expansion)	Reduced clarity due to opacity	increases thermal, acid, and shear resistance	Reduce or mixed, depending on crosslink type	[52]

#### Carboxymethylation:

Carboxymethylated starch (CMS) introduces hydrophilic carboxymethyl groups, disrupting internal hydrogen bonding, decreasing crystallinity, and increasing swelling and solubility [17]. This enhances microbial resistance and improves paste clarity. However, CMS has limited thermal resistance, especially under HPHT conditions, making it suitable only when combined with cross-linking agents [17].

#### Acetylation:

Acetylation substitutes hydroxyl groups with acetyl groups, reducing gelatinization temperature and energy requirement [47]. It produces a moderately rough morphology while maintaining granule integrity. Acetylated starches form transparent pastes and exhibit improved freeze-thaw and storage stability, making them suitable for saline and moderately hot conditions [48].

#### Succinylation (OSA):

Succinylated starches offer enhanced emulsifying capacity and cold stage stability due to increased molecular repulsion and structural rearrangements [49]. Their swelling capacity and clarity are superior, making them suitable for dual-function additives in drilling fluids requiring filtration control and emulsification.

#### Oxidation:

Oxidized starches possess a lower molecular weight due to partial depolymerization, enhancing solubility and clarity. Their effectiveness in film applications is well-documented [51], but data regarding their drilling-fluid behavior is limited. Further exploration is necessary to validate their use under dynamic wellbore conditions.

#### Cross-linking:

Cross-linked starches maintain or increase crystallinity, reinforcing granule structure and boosting resistance to thermal, mechanical, and chemical stress. This modification raises gelatinization temperatures while reducing swelling and solubility, which helps maintain viscosity in HPHT environments [52].

## 4. Applications of modified polymers as drilling fluid additives

Modifying polymers is a common approach to enhance their functional properties, and starch modification has attracted significant attention to improve its performance across various industries, including drilling fluids. This study examines the physicochemical characteristics and drilling fluid behavior of five chemically modified starches: carboxymethylation, acetylation, succinylation (OSA), oxidation, and cross-linking. By reviewing existing literature and comparing data, it explores how each modification impacts critical properties such as crystallinity, swelling,

gelatinization, solubility, retrogradation, and thermal stability. Additionally, their rheological performance in drilling fluids is assessed through parameters like apparent viscosity (AV), plastic viscosity (PV), yield point (YP), gel strength, and fluid loss control [53]. The results highlight that dual-modified and cross-linked starches exhibit superior stability under high-pressure, high-temperature (HPHT) conditions, while carboxymethylated and acetylated starches perform well in moderate drilling environments. Oxidized starch remains relatively underexplored in drilling applications. This work aims to guide the selection and development of starch-based additives for optimized drilling fluid performance.

Table 3 consolidates experimental findings from the literature on the rheological properties of modified starches in drilling mud systems.

**Table 3** Impact of Starch Modifications on Drilling Fluids

Modification	Apparent Viscosity (AV)	Plastic Viscosity (PV)	Yield Point / Gel Strength	Fluid Loss Control / Filtrate Reduction	Temperature & Salt Resistance	Key References
Carboxymethylation (CMC)	AV increases modestly with modified tapioca starch vs native starch	PV rises (consistency index $\uparrow$ from $\sim 5.6$ to $15.1$ depending on concentration)	YP increases; Gel strength improved in a dose-dependent manner	Filtrate loss reduced vs native starch; HTHP fluid loss lower	Moderate thermal stability CMC degrades under HPHT (e.g., viscosity drop after $302^\circ\text{F}$ ) unless dual-modified	[53,54]
Acetylation	AV relatively stable; some formulations (AC) show the highest dial readings post-aging	PV is maintained or increased after hot rolling for AC and CC types	YP & Gel strength retained or improved under HPHT with AC and cross-linked starches	Fluid loss control is adequate; AC shows acceptable filtrate reduction in HPHT	Superior HPHT performance than CMC; chains remain intact after aging at $302^\circ\text{F}$	[55]
Cross-linking (STMP, etc.)	AV shows minimal increase; maintains viscosity under HPHT stress	PV moderate ( $\sim 33.5\text{ mPa}\cdot\text{s}$ at $1.5\%$ starch at $160^\circ\text{C}$ )	YP and gel strength are preserved under high temperature; dual-modified CMITS shows higher YP and GS	Very effective filtration loss control: API fluid loss $\sim 11\text{ mL}$ at $160^\circ\text{C}$ ( $1.5\%$ dosage)	Excellent thermal and salt resistance; filtration maintained at $150\text{--}160^\circ\text{C}$	[56]
Dual-modification (CM + irradiation)	Non-Newtonian shear-thinning behavior; AV enhanced at elevated temperatures & salts	PV increased with high DS ( $\sim 0.66$ ) and concentration ( $\sim 8\text{ ppb}$ )	YP & GS significantly improved under HPHT and saline conditions	Filtrate performance retained; optimal mud cleaning behavior suggested	Best temperature and salt resistance among all modifications tested	[53]

Oxidation (e.g., oxidized starch)	Research is lacking for drilling fluids specifically; general rheology improvements documented in food films do not apply to the mud context.	Gel strength/Yield point data in the drilling fluid context is absent	No direct drilling-fluid data; more studied in film applications	Data not available; fluid loss control by oxidized starch in drilling is unexplored	Not evaluated in drilling-fluid literature	[57]
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Critical evaluation of Tables 2 and 3 reveals the functional strengths and limitations of each modification concerning drilling fluid applications:

- High-Performance (HPHT Ready)

Cross-linked and Dual-modified starches show the highest resistance to thermal degradation, maintain viscosity under stress, and effectively reduce fluid loss. These are best suited for high-temperature and high-pressure environments.

- Moderate-Performance (Field-Applicable)

Acetylated and Carboxymethylated starches offer reasonable thermal stability and good fluid-loss performance. However, they may require a combination with other additives or secondary modifications for deeper wells.

- Emerging or Experimental

Oxidized starches possess beneficial physicochemical traits but lack robust drilling fluid data. They hold promise for future biodegradable drilling fluid systems pending further investigation.

Hence, the understanding of each modified starch category aids in matching it with specific drilling challenges, optimizing additive selection, and encouraging further innovation in starch modification technologies.

## 5. Conclusion

This review has demonstrated that using modified natural polymers (specifically cellulose and starch) is essential for enhancing the performance of water-based drilling fluids, particularly in the face of diverse drilling challenges such as high temperature, high pressure, and complex formation conditions. Crucial findings include:

- Limitations of Native Polymers: Unmodified cellulose and starch exhibit limited thermal stability, low solubility in aqueous systems, and poor rheological resilience. These limitations hinder their standalone performance in deep-well and HPHT drilling conditions.
- Effectiveness of Modification: Chemical modification techniques significantly improve starch's structural and functional attributes. These enhancements include increased swelling capacity, solubility, thermal stability, and resistance to retrogradation. Cross-linking, in particular, reinforces granule stability and offers excellent thermal and mechanical degradation resistance.
- Rheological Improvements: Modified starches, especially dual-modified and cross-linked variants, demonstrate superior rheological behavior, maintaining apparent viscosity, plastic viscosity, and gel strength under HPHT and saline conditions. These modifications also substantially improve fluid loss control, a critical parameter in drilling efficiency and wellbore stability.

Therefore, the strategic modification of cellulose and starch expands their utility as multifunctional, eco-friendly drilling fluid additives. Future research should aim to develop more targeted, hybrid, or synergistic modification strategies that combine chemical and physical techniques to meet the increasing demands of complex drilling environments. Additionally, greater emphasis should be placed on field validation of underutilized modifications, such as oxidized starches, to fully leverage the potential of natural polymers in petroleum engineering applications.

## Compliance with ethical standards

### Disclosure of conflict of interest

The author declares no conflict of interest to be disclosed.

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